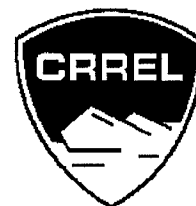


98-4

SPECIAL REPORT



## Overview of On-Site Analytical Methods for Explosives in Soil

Alan B. Crockett, Thomas F. Jenkins, Harry D. Craig,  
and Wayne E. Sisk

February 1998

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**Abstract:** On-site methods for explosives in soil are reviewed. Current methods emphasize the detection of TNT and RDX. Methods that have undergone significant validation fall into two categories: colorimetric-based methods and enzyme immunoassay methods. Discussions include considerations of specificity, de-

tection limits, extraction, cost, and ease of use. A discussion of the unique sampling design considerations is also provided as well as an overview of the most commonly employed laboratory method for analyzing explosives in soil. A short summary of ongoing development activities is provided.

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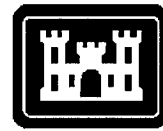
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# Special Report 98-4



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February 1998

Prepared for  
OFFICE OF THE CHIEF OF ENGINEERS

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## PREFACE

This report was prepared by Alan B. Crockett, Idaho National Engineering and Environmental Laboratory, Lockheed Martin Idaho Technologies Company, Idaho Falls, Idaho; Dr. Thomas F. Jenkins, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire; Harry D. Craig, U.S. Environmental Protection Agency, Region 10, Portland, Oregon; and Wayne E. Sisk, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland.

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# Overview of On-Site Analytical Methods for Explosives in Soil

ALAN B. CROCKETT, THOMAS F. JENKINS, HARRY D. CRAIG, AND WAYNE E. SISK

## INTRODUCTION

The purpose of this report is to survey the current status of field sampling and on-site analytical methods for detecting and quantifying secondary explosives compounds in soils (Table 1). The paper also includes a brief discussion of EPA Method 8330 (EPA 1995), the reference analytical method for the determination of 14 explosives and co-contaminants in soil.

This report is divided into the following major sections: introduction; background; an overview of sampling and analysis for explosives in soil; data quality objectives; unique sampling design considerations for explosives; procedures for statistically comparing on-site and reference analytical methods; a summary of on-site analytical methods; and a summary of the current EPA reference analytical method, Method 8330 (EPA 1995). Although some sections may be used independently, joint use of the field sampling and on-site analytical methods sections is recommended to develop a sampling and analytical approach that achieves project objectives.

Many of the explosives listed in Table 1 are not specific target compounds of screening methods, yet they may be detected by one or more screening methods because of their similar chemical structure. Also listed are the explosives and propellant compounds targeted by high performance liquid chromatography (HPLC) methods, including EPA SW-846 Method 8330, the standard method required by EPA regions for laboratory confirmation.

## BACKGROUND

Evaluating sites potentially contaminated with explosives is necessary to carry out U.S. Department of Defense, EPA, and U.S. Department of

Energy policies on site characterization and remediation under the Superfund, Resource Conservation and Recovery Act (RCRA), Installation Restoration, Base Closure, and Formerly Used Defense Site environmental programs. Facilities that may be contaminated with explosives include, for example, active and former manufacturing plants, ordnance works, Army ammunition plants, Naval ordnance plants, Army depots, Naval ammunition depots, Army and Naval proving grounds, burning grounds, artillery impact ranges, explosive ordnance disposal sites, bombing ranges, firing ranges, and ordnance test and evaluation facilities.

Historical disposal practices from manufacturing, spills, ordnance demilitarization, lagoon disposal of explosives-contaminated wastewater, and open burn/open detonation (OB/OD) of explosives sludges, waste explosives, excess propellants, and unexploded ordnance often result in soils contamination. Common munitions fillers and their associated secondary explosives include Amatol (ammonium nitrate/TNT), Baratol (barium nitrate/TNT), Cyclonite or Hexogen (RDX), Cyclotols (RDX/TNT), Composition A-3 (RDX), Composition B (TNT/RDX), Composition C-4 (RDX), Explosive D or Yellow D (AP/PA), Octogen (HMX), Octols (HMX/TNT), Pentolite (PETN/TNT), Picratol (AP/TNT), tritonal (TNT), tetrytols (tetryl/TNT), and Torpex (RDX/TNT).

Propellant compounds include DNTs and single-base (NC), double-base (NC/NG), and triple-base (NC/NG/NQ) smokeless powders. In addition, NC is frequently spiked with other compounds (e.g., TNT, DNT, DNB) to increase its explosive properties. AP/PA is used primarily in Naval munitions such as mines, depth charges, and medium-to-large caliber projectiles. Tetryl is used primarily as a boosting charge, and PETN is used in detonation cord.

A number of munitions facilities have high lev-

**Table 1. Analytical methods for commonly occurring explosives, propellants, and impurities/degradation products.**

<i>Acronym</i>	<i>Compound name</i>	<i>Field method</i>	<i>Laboratory method</i>
TNT	2,4,6-trinitrotoluene	Cp, Ip	N
TNB	1,3,5-trinitrobenzene	Cs, Is	N
DNB	1,3-dinitrobenzene	Cs	N
2,4-DNT	2,4-dinitrotoluene	Cp, Cs	N
2,6-DNT	2,6-dinitrotoluene	Cs, Is	N
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	Cs	N
2-AmDNT	2-amino-4,6-dinitrotoluene		N
4-AmDNT	4-amino-2,6-dinitrotoluene	Is	N
NT	Nitrotoluene (3 isomers)		N
NB	Nitrobenzene		N
<b>Nitramines</b>		Cs	N
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	Cp, Ip	N
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	Cs	N
NQ	Nitroguanidine	Cs	G
<b>Nitrate esters</b>		Cs	
NC	Nitrocellulose	Cs	*L
NG	Nitroglycerin	Cs	*P
PETN	Pentaerythritol tetranitrate	Cs	*P
<b>Ammonium picrate/picric acid</b>			
AP/PA	Ammonium 2,4,6-trinitrophenoxide/2,4,6-trinitrophenol	Cp, Is	A

Cp = Colorimetric field method, primary target analyte(s).

Cs = Colorimetric field method, secondary target analyte(s).

Ip = Immunoassay field method, primary target analyte(s).

Is = Immunoassay field method, secondary target analyte(s).

N = EPA SW-846, Nitroaromatics and Nitramines by HPLC, Method 8330 (EPA 1995a).

P = PETN and NG (Walsh unpublished CRREL method).

G = Nitroguanidine (Walsh 1989).

L = Nitrocellulose (Walsh unpublished CRREL method).

A = Ammonium picrate/picric acid (Thorne and Jenkins 1995a).

\*The performance of a number of field methods has not been assessed utilizing "approved" laboratory methods. It is recommended that verification of the performance of any analytical method be an integral part of a sampling/analysis projects quality assurance program.

els of soil and groundwater contamination, although on-site waste disposal was discontinued 20 to 50 years ago. Under ambient environmental conditions, explosives are highly persistent in soils and groundwater, exhibiting a resistance to naturally occurring volatilization, biodegradation, and hydrolysis. Where biodegradation of TNT occurs, 2-AmDNT and 4-AmDNT are the most commonly identified transformation products. Photochemical decomposition of TNT to TNB occurs in the presence of sunlight and water, with TNB being generally resistant to further photodegradation. TNB is subject to biotransformation to 3,5-dinitroaniline, which has been recommended as an additional target analyte in EPA

Method 8330. Picrate is a hydrolysis transformation product of tetryl, and is expected in environmental samples contaminated with tetryl. Site investigations indicate that TNT is the least mobile of the explosives and most frequently occurring soil contamination problem. RDX and HMX are the most mobile explosives and present the largest groundwater contamination problem. TNB, DNTs, and tetryl are of intermediate mobility and frequently occur as co-contaminants in soil and groundwater. Metals are co-contaminants at facilities where munitions compounds were handled, particularly at OB/OD sites. Field analytical procedures for metals, such as x-ray fluorescence, may be useful in screening soils for



metals in conjunction with explosives at munitions sites.

The frequency of occurrence of specific explosives in soils was assessed by Walsh et al. (1993), who compiled analytical data on soils collected from 44 Army ammunition plants, arsenals, and depots, and two explosive ordnance disposal sites. Of the 1155 samples analyzed by EPA Method 8330, 319 samples (28%) contained detectable levels of explosives. The frequency of occurrence and the maximum concentrations detected are shown in Table 2. TNT was the most commonly occurring compound in contaminated samples; it was detected in 66% of the contaminated samples and in 80% of the samples if the two explosive ordnance disposal sites are excluded. Overall, either TNT or RDX or both were detected in 72% of the samples containing explosives residues, and 94% if the ordnance sites are excluded. Thus, by screening for TNT and RDX at ammunition plants, arsenals, and depots, 94% of the contaminated areas could be identified (80% if only TNT was determined). This demonstrates the feasibility of screening for one or two compounds or classes of compounds to identify the initial extent of contamination at munitions sites. The two ordnance sites were predominantly contaminated with DNTs, probably from improper detonation of waste propellant. The table also shows that NB and NTs were not detected in these samples; however, NTs are found in waste produced from the manufacture of DNT.

**Table 2. Occurrence of analytes detected in soil contaminated with explosives.**

<i>Compound</i>	<i>Sample with analyte present (%)</i>	<i>Maximum level (µg/g)</i>
<b>Nitroaromatics</b>		
TNT	66	102,000
TNB	34	1790
DNB	17	61
2,4-DNT	45	318
2,6-DNT	7	4.5
2-AmDNT	17	373
4-AmDNT	7	11
Tetryl	9	1260
<b>Nitramines</b>		
RDX	27	13,900
HMX	12	5700
TNT and/or RDX	72	

Derived from Walsh et al. (1993).

## OVERVIEW OF SAMPLING AND ANALYSIS FOR EXPLOSIVES IN SOIL

The environmental characteristics of munitions compounds in soil indicate that they are extremely heterogeneous in spatial distribution. Concentrations range from nondetectable levels (<0.5 parts per million [ppm]) to percent levels (>10,000 ppm) for samples collected within several feet of each other. Some waste disposal practices, such as OB/OD, exacerbate the problem at these sites and may result in conditions ranging from no soil contamination up to solid "chunks" of bulk secondary explosives, such as TNT or RDX. Secondary explosives concentrations above 10% (>100,000 ppm) in soil are also of concern from a potential reactivity standpoint and may affect sample and materials handling processes during remediation. An explosives hazard safety analysis is needed for materials handling equipment to prevent initiating forces that could propagate a detonation throughout the soil mass.

Reliance on laboratory analyses only for site characterization may result in a large percentage of samples (up to 80%, depending upon the site) with nondetectable levels. The remaining samples may indicate concentrations within a range of four orders of magnitude. Analyzing a small number of samples at an off-site laboratory may result in inadequate site characterization for estimating soil quantities for remediation and may miss potentially reactive material. Laboratory analytical costs vary depending on required turnaround time. Typical costs for EPA Method 8330 analysis range from \$250 to \$350 per sample for 30-day turnaround, \$500 to \$600 for 7-day turnaround, and approximately \$1000 per sample for 3-day turnaround, if it is available.

Because of the extremely heterogeneous distribution of explosives in soils, on-site analytical methods are a valuable, cost-effective tool to assess the nature and extent of contamination. Because costs per sample are lower, more samples can be analyzed and the availability of near-real-time results permits redesign of the sampling scheme while in the field. On-site screening also facilitates more effective use of off-site laboratories using more robust analytical methods. Even if only on-site methods are used to determine the presence or absence of contamination (i.e., all positive samples are sent off-site for laboratory analysis), analytical costs can be reduced considerably. Because on-site methods provide near-real-time feedback, the results of screening can be used to

focus additional sampling on areas of known contamination, thus possibly saving additional mobilization and sampling efforts. This approach has been successfully used for a Superfund remedial investigation of an OB/OD site (Craig et al. 1993).

During site remediation, such as Superfund remedial actions, data are needed on a near-real-time basis to assess the progress of cleanup. On-site methods can be used during remediation to guide excavation and materials handling activities and to evaluate the need for treatment on incremental quantities of soil (EPA 1992b). Final attainment of soil cleanup levels should be determined by an approved laboratory method, such as EPA Method 8330. This approach was effectively used at a Superfund remedial action for an explosives wash-out lagoon (Oresik et al. 1994, Markos et al. 1995).

## DATA QUALITY OBJECTIVES

The EPA Data Quality Objectives process is designed to facilitate the planning of environmental data collection activities by specifying the intended use of the data (what decision is to be made), the decision criteria (action level), and the tolerable error rates (EPA 1994, ASTM 1996). Integrated use of on-site and laboratory methods for explosives in soil helps to achieve such objectives as determining the horizontal and vertical extent of contamination, obtaining data to conduct a risk assessment, identifying candidate wastes for treatability studies, identifying the volume of soil to be remediated, determining whether soil presents a potential detonation hazard (reactive according to RCRA regulations), and determining whether remediation activities have met the cleanup criteria.

Environmental data such as rates of occurrence, average concentrations, and coefficients of variation are typically highly variable for contaminants associated with explosives sites. These differences are a function of fate and transport properties, occurrence in different media, and interactions with other chemicals, in addition to use and disposal practices. Information on frequency of occurrence and coefficient of variation determines the number of samples required to adequately characterize exposure pathways and is essential when designing sampling plans. Low frequencies of occurrence and high coefficients of variation, such as with explosives, mean that more samples will be required to characterize the exposure pathways of interest. Sampling variability typically

contributes much more to total error than analytical variability (EPA 1990, 1992a). Under these conditions, the major effort should be to reduce sampling variability by taking more samples using less expensive methods (EPA 1992a).

EPA's Guidance for Data Useability in Risk Assessment (EPA 1992a) indicates that on-site methods can produce legally defensible data if appropriate method quality control is available and if documentation is adequate. Field analyses can be used to decrease cost and turnaround time as long as supplemental data are available from an analytical method capable of quantifying multiple explosives analytes (e.g., Method 8330) (EPA 1992a). Significant quality assurance oversight of field analysis is recommended to enable the data to be widely used. The accuracy (correctness of the concentration value and a combination of both systematic error [bias] and random error [precision]) of on-site measurements may not be as high in the field as in fixed laboratories, but the quicker turnaround and the possibility of analyzing a larger number of samples more than compensates for this factor. Remedial project managers, in consultation with chemists and quality assurance personnel, should set accuracy levels for each method and proficiency standards for the on-site analyst.

On-site methods may be useful for analysis of waste treatment residues, such as incineration ash, compost, and bioslurry reactor sludges. However, on-site methods should be evaluated against laboratory methods on a site- and matrix-specific basis because of the possibility of matrix interference. Treatability studies are used to evaluate the potential of different treatment technologies to degrade target and intermediate compounds and to evaluate whether cleanup levels may be achieved for site remediation. Treatability study waste for explosives-contaminated soils should be of higher-than-average concentration to evaluate the effects of heterogeneous concentrations and the potential toxicity effects for processes such as bioremediation.

During remediation of soils contaminated with explosives, it is necessary to monitor the rate of degradation and determine when treatment criteria have been met so that residues below cleanup levels can be disposed of and additional soil treated. Soils contaminated with explosives are currently being treated by incineration, composting, and solidification/stabilization (Noland et al. 1984, Turkeltaub et al. 1989, EPA 1993, Craig and Sisk 1994, Miller and Anderson 1995, Channell et al. 1996). Other biological treat-

ment systems that have been evaluated for treating explosives-contaminated soils include anaerobic bioslurry, aerobic bioslurry, white rot fungus, and landfarming (Craig et al. 1995, Sundquist et al. 1995).

## UNIQUE SAMPLING DESIGN CONSIDERATIONS FOR EXPLOSIVES

### Heterogeneity problems and solutions

The heterogeneous distribution of explosives in soil is often alluded to but seldom quantified. The problem is probably considerably greater for explosives residues in soil than for most other organic waste. According to available Superfund site data, the median coefficient of variation (CV) (standard deviation divided by the mean) for volatiles, extractables, pesticides/polychlorinated biphenyls (PCBs), and tentatively identified compounds in soils ranges from 0.21 to 54% for individual contaminants (EPA 1992b). Data from 11 munitions sites show the median CV for TNT was 284%, and the TNT CV ranged from 127% to 335% for individual sites. Comparable data for RDX show a median CV of 137% with a range of 129% to 203%; the median CVs for 2,4-DNT, AP/PA, and PETN were 414%, 184%, and 178%, respectively. If the natural variability of the chemicals of potential concern is large (e.g., CV >30%), the major planning effort should be to collect more environmental samples (EPA 1992b).

Jenkins et al. (1996a, b) recently conducted studies to quantify the short-range sampling variability and analytical error of soils contaminated with explosives. Nine locations (three at each of three different facilities) were sampled. At each location, seven core samples were collected from a circle with a radius of 61 cm: one from the center and six equally spaced around the circumference. The individual samples and a composite sample of the seven samples were analyzed in duplicate, on-site, using the EnSys RISC colorimetric soil test kit for TNT (on-site method) and later by Method 8330 at an off-site laboratory. Results showed extreme variation in concentration at five of the nine locations, with the remaining four locations showing more modest variability. For sites with modest variability, only a small fraction of the total error was because of analytical error, i.e., field sampling error dominated total error. For the locations showing extreme short-range heterogeneity, sampling error overwhelmed analytical error. Contaminant distributions were very site-specific, dependent on

a number of variables such as waste disposal history, the physical and chemical properties of the specific explosive, and the soil type. The conclusion was that, to improve the quality of site characterization data, the major effort should be placed on the use of higher sampling densities and composite sampling strategies to reduce sampling error.

In a subsequent study at an HMX-contaminated antitank firing range, similar short-range heterogeneity was observed (Jenkins et al. 1997). At both the short- and mid-scale, sampling error overwhelmed analytical error. It was observed that the particulate nature of these contaminants in near-surface soils is a major contributor to substantial spatial heterogeneity in distribution.

There are several practical approaches to reducing overall error during characterization of soils contaminated with explosives, including increasing the number of samples or sampling density, collecting composite samples, using a stratified sampling design, and reducing within-sample heterogeneity. Because explosives have very low volatility, loss of analytes during field preparation of composite samples is not a major concern.

### *Increasing the number of samples*

One simple way to improve spatial resolution during characterization is by collecting more samples using a finer sampling grid, such as a 5-m grid spacing instead of a 10-m spacing. Though desirable, this approach has been rejected in the past because of the higher sampling and analytical laboratory costs. When inexpensive on-site analytical methods are used, this approach becomes feasible. The slightly lower accuracy associated with on-site methods is more than compensated for by the greater number of samples that can be analyzed and the resultant reduction in total error.

### *Collection of composite samples*

The collection of composite samples is another very effective means of reducing sampling error. Samples are always taken to make inferences to a larger volume of material, and a set of composite samples from a heterogeneous population provides a more precise estimate of the mean than a comparable number of discrete samples. This occurs because compositing is a "physical process of averaging" (adequate mixing and subsampling of the composite sample are essential to most compositing strategies). Averages of samples have greater precision than the individual samples.

Decisions based on a set of composite samples will, for practical purposes, always provide greater statistical confidence than for a comparable set of individual samples. In the study discussed above by Jenkins et al. (1996a, b; 1997), the composite samples were much more representative of each plot than the individual samples that made up the composites. Using a composite sampling strategy usually allows the total number of samples analyzed to be reduced, thereby reducing costs while improving characterization. Compositing should be used only when analytical costs are significant. An American Society for Testing and Materials (ASTM) guide was developed on composite sampling and field subsampling (Gagner and Crockett 1996, ASTM 1997).

#### *Stratified sampling designs*

Stratified sampling may also be effective in reducing field and subsampling errors. Using historical data and site knowledge or results from preliminary on-site methods, it may be possible to identify areas in which contaminant concentrations are expected to be moderately heterogeneous (pond bottom) or extremely heterogeneous (open detonation sites). Different compositing and sampling strategies may be used to characterize different areas, thereby increasing the likelihood of a more efficient characterization.

Another means of stratification is based on particle size. Because explosives residues often exist in a wide range of particle sizes (crystals to chunks), it is possible to sieve samples into various size fractions that may reduce heterogeneity. If large chunks of explosives are present, it may be practical to coarse-sieve a relatively large sample (many kilograms), medium-sieve a portion of those fines, and subsample the fines from medium screening as well. This would yield three samples of different particle size and presumes that heterogeneity increases with coarseness. Each fraction would be analyzed separately but not necessarily by the same method (visual screening of the coarser fractions for chunks of explosives may be possible) and then could be summed to yield the concentration on a weight or area basis. In addition, aqueous disposal of explosives wastewaters, such as those found in washout lagoons or at spill sites, often results in preferential sorption to fine-grained materials, such as fines or clays, particularly for nitroaromatics.

#### *Reducing within-sample heterogeneity*

The heterogeneity of explosives in soils is fre-

quently observed during the use of on-site analytical methods in which duplicate subsamples are analyzed and differ by more than an order of magnitude. Grant et al. (1993) conducted a holding time study using field-contaminated soils that were air-dried, ground with a mortar and pestle, sieved, subsampled in triplicate, and analyzed using Method 8330. Even with such sample preparation, the results failed to yield satisfactory precision. (The relative standard deviations [RSDs] often exceeded 25%, compared with RSDs below 3% at two other sites.) Subsampling in the field is much more challenging because complete sample processing is not feasible. However, most screening procedures specify relatively small samples, typically a few grams.

To reduce within-sample heterogeneity, two methods can be employed: either homogenization and extraction or analysis of a larger sample. Unless directed otherwise, an analyst should assume that information representative of the entire contents of the sample container is desired. Therefore, the subsample extracted or directly analyzed should be representative of the container. The smaller the volume of that subsample removed for analysis and extraction, the more homogeneous the entire sample should be before subsampling (e.g., a representative 0.5-g subsample is more difficult to obtain than a 20-g subsample from a 250-g sample). Collecting representative 2-g subsamples from 300 g of soil is difficult and can require considerable sample processing, such as drying, grinding, and riffle splitting. Even in the laboratory, as discussed above, obtaining representative subsamples is difficult. An ASTM guide has been developed to help in this regard (Gagner and Crockett 1996). Although sample-mixing procedures such as sieving to disaggregate particles, mixing in plastic bags, etc., can and should be used to prepare a sample, extracting a larger sample is perhaps the easiest method of improving representativeness. For this reason, 20 g of soil is extracted for the Cold Regions Research and Engineering Laboratory (CRREL) method, and the same approach may easily be used to improve results with most of the on-site methods shown in Table 3. The major disadvantage of extracting the larger sample is the larger volume of waste solvent and solvent-contaminated soil that needs disposal.

The effectiveness of proper mixing in the field is illustrated in the recent reports by Jenkins et al. (1996a, b; 1997). Duplicate laboratory analyses of the same samples, including drying, grinding,

Table 3. Comparative data for selecting on-site analytical methods for explosives in soil\*.

Method/ Kit	Method type, analytes, and EPA Method No.	Detection range and range factor	Type of results	Samples per batch	Soil sample size	Sample preparation and extraction	Analysis time— predictions rate (one person)
CRREL	Colorimetric TNT, RDX, 2,4-DNT, Ammonium picrate/ picric acid	TNT: 1 to 22 mg/kg (20x) RDX: 1 to 20 mg/kg (20x) 2,4-DNT: 2 to 20 mg/kg (10x) AP/PA: 1.3 to 69 mg/kg (53x)	TNT, RDX: Quantitative 2,4-DNT: Semiquantitative AP/PA: Quantitative	TNT: Batch or single RDX: 6 to 7/batch or single 2,4-DNT and AP/PA: Single or batch	20 g	3 min shaking in 100 mL acetone; settling; filtration.	30 minute extract/6 samples; TNT: 5 minutes/sample; RDX: 30 minutes/6 RDX samples; 25 samples/day for TNT + RDX; DNT: 30 minutes/6 samples; AP/PA: 15 minutes/sample.
EnSys RISC	Colorimetric TNT: Method 8515 draft RDX: Method 8510 proposed	TNT: 1 to 30 mg/kg (30x) RDX: 1 to 30 mg/kg (30x)	Quantitative	Single	10 g	Dry <10% moisture (optional); 3 min shaking in 50 mL acetone; 5 min settling; filtration.	TNT: 30 to 35 minutes/10 samples in lab; estimated 40 to 45 minutes in field. RDX: 60 minutes/6 samples. Op- tional drying time not included.
USACE	Colorimetric TNT	6 to 100 mg/kg (17x)	Quantitative	Single or batch	6 g	1 min shaking in 35 mL methanol; settling; filtration as needed.	10 to 20 samples/day depend- ing on soil characteristics.
ENVIROL	Colorimetric TNT	3 to 100 mg/kg (33x)	Quantitative	Single or batch	10 g	5 min shaking with 10 mL of methanol; settling; solid phase extraction using hexane; liquid- liquid transfer	30 min per sample
DTECH	Immunoassay—ELISA TNT: Method 4050 draft RDX: Method 4051 draft	TNT: 0.5 to 5.0 mg/kg (10x) RDX: 0.5 to 6.0 mg/kg (12x)	Semiquantitative (concentration range)	4 (single or batch)	3 mL ~4.5 g	3 min shaking in 6.5 mL acetone; settle 1 to 10 min.	30 minutes for 1 to 4 samples for TNT or RDX.
Idetek Quantix	Immunoassay—ELISA Antigen-Antibody TNT	TNT: 0.25 to 100 mg/kg (400x)	Quantitative	20 to 40 (batch only)	~4.2 g	3 min shaking in 21 mL acetone; settle several minutes.	2.5 to 3.5 hours for 20 to 40 samples. Idetek estimates—2 hours for up to 40 TNT samples.
EnviroGard	Immunoassay—ELISA TNT: Plate kit TNT: Soil (tube) kit	Plate kit: 1 to 100 mg/kg (100x) Tube kit: 0.2 to 15 mg/kg (75x)	Plate: Quantitative Tube: Semiquantitative (concentration range)	Plate: batch of 8 Tube: batch of 14	2 g	Air-dry soil, 2 min shaking in 8 mL acetone; filter.	Plate: 90 minutes for 8 samples Tube: 30 minutes for 14 samples Drying time not included.
Ohmicron RaPID Assay	Immunoassay—ELISA Magnetic particle/tube kit TNT: Method 4050 proposed	TNT: 0.07 to 5 mg/kg (71x)	Quantitative	5 to 51 (batch only)	10 g	1 min shaking in 20 mL methanol; settle 5 min; filter.	1 hour for 20 extractions; 45 minutes for analysis (51 samples).

\*Expanded and modified from EPA 1997.

Table 3. Comparative data for selecting on-site analytical methods for explosives in soil\* (continued).

Method/ Kit	Interferences and cross-reactivities >1% based on $IC_{50}$ (see text)	Recommended QA/QC	Storage conditions and shelf life of kit or reagents	Skill level
CEREL	TNT = TNT + TNB + DNB + DNTs + tetryl; - detection limits (ppm); TNB <0.5; 2,4-DNT 0.5; 2,6-DNT 2.1; tetryl 0.9 RDX = RDX + HMX + PETN + NQ + NC + NG - detection limits (ppm); HMX 2.4; PETN 1; NQ 10; NC 42; NG 9 Soil moisture >10% and humics interfere with TNT and RDX; nitrate and nitrite interfere with RDX. 2,4-DNT = 2,4-DNT + 2,6-DNT + TNT + TNB + tetryl; high copper, moisture, and humics interfere. AP/PA = relatively free of humic and nitroaromatic interferences.	Blank and calibration standards analyzed daily before and after sample analyses. Blank and spiked soil run daily.	Store at room temperature.	Medium
EnSys RISC	TNT = TNT + TNB + DNB + DNTs + tetryl; - detection limits (ppm); TNB <0.5; 2,4-DNT 0.5; 2,6-DNT 2.1; tetryl 0.9 RDX = RDX + HMX + PETN + NQ + NC + NG - detection limits (ppm); HMX 2.4; PETN 1; NQ 10; NC 42; NG 9 Soil moisture >10% and humics interfere with TNT and RDX; nitrate and nitrite interfere with RDX.	Method and soil blanks and a control sample daily, one duplicate/20 samples. Some positive field results (1:10) should be confirmed.	Store at room temperature. Shelf life: TNT = 2 to 24 months at 27°C RDX = 2 to 12 months at 27°C	TNT: Low RDX: Medium
USACE	TNB interferes by raising minimum detection limit.	Blank soil sample, and calibration standard prepared from clean site soil.	Store at room temperature.	Medium
ENVIROL	Tetryl is a negative interference and the DNTs are a positive interference.	Two calibration standards; blank solution; control sample.	Recommended storage 20°C Acceptable range 4–30°C Shelf life: 3 months if kept below 25°C	Medium
DTECH	Cross reactivity: TNT: tetryl = 35%; TNB = 23%; 2-AmDNT = 11%; 2,4-DNT = 4%; AP/PA unknown but ~100% at lower limit of detection. RDX: HMX = 3%	Samples testing positive should be confirmed using standard methods.	Store at room temperature or refrigerate; do not freeze or exceed 37°C for prolonged period. Shelf life 9 months at room temperature.	Low
Idetek Quantix	Cross reactivity: TNB = 47%; tetryl = 6.5%; 2,4-DNT = 2%; 4-AmDNT = 2%	Duplicate extractions; 1 in 10 replicate; 2 sample wells/extract.	Refrigerate 2° to 8°C, do not freeze or exceed 37°C. Shelf life 9 to 12 months. Avoid direct light.	Medium-high, initial training recommended
EnviroGard	Cross reactivity: Plate: 4-AmDNT = 41%; 2,6-DNT = 41%; TNB = 7%; 2,4-DNT = 2% Tube: 2,6-DNT = 20%; 4-AmDNT = 17%; TNB = 3%; 2,4-DNT = 2%	Plate: Samples run in duplicate.	Store 4° to 8°C; do not freeze or exceed 37°C. Do not expose substrate to direct sunlight. Shelf life: Plate 3 to 14 months Tube 3 to 6 months	Plate: Medium-high Tube: Medium
Ohmicron RAPID Assay	Cross reactivity: TNB = 65%; 2,4-Dinitroaniline = 6%; tetryl = 5%; 2,4-DNT = 4%; 2-AmDNT = 3%; DNB = 2%	Duplicate standard curves; positive control sample supplied. Positive results requiring action may need confirmation by another method.	Refrigerate reagents 2° to 8°C. Do not freeze. Shelf life 3 to 12 months.	Medium-high initial training recommended

\*Expanded and modified from EPA 1997.

Table 3. Comparative data for selecting on-site analytical methods for explosives in soil\* (continued).

Method/ Kit	Training availability	Costs (not including labor)	Comparisons to Method 8330 references	Other references	Developer information	Additional considerations
CRREL	Free video for TNT and RDX; see text for address. None available for 2,4-DNT, AP/PA.	\$15/sample plus \$1500 for Hach spectrometer.	Brouillard et al. 1993; EPA 1993, 1995a (Method 8515), 1995b; Jenkins 1990; Jenkins and Walsh 1992; Markos et al. 1995; Lang et al. 1990; Walsh and Jenkins 1991; Jenkins et al. 1996a; Jenkins and Walsh 1991, 1992; Thorne and Jenkins 1995a	Jenkins et al. 1995; Thorne and Jenkins 1995b	Dr. Thomas F. Jenkins CRREL 72 Lyme Road Hanover, NH 03755-1290 (603) 646-4385	Large work area (2 large desks); requires the most setup time; possible TNB interference; no electricity or refrigeration required; deionized water required; must assemble materials; glassware must be rinsed between analyses; larger volume of acetone waste; color indicative of compounds.
EnSys Risc	Training available. Applicable video on CRREL method available, address in text.	\$21/sample for TNT, \$25/sample for RDX plus \$160/day or \$430/wk for lab station. Lab station cost = \$1950.	EPA 1995 (Method 8515); EPA 1997; IT 1995; Jenkins et al. 1996a, 1996b; Markos et al. 1995; Myers et al. 1994		Strategic Diagnostics, Inc. 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	Large work area (desk size); power supply required to charge Hach spectrometer; possible TNB interference; color indication of other compounds; requires acetone and deionized water; cuvettes must be rinsed between analyses. Nitrate and nitrite interferences with RDX kit can be corrected using alumin-a-cartridges from EnSys.
USACE	None available.	\$4/sample or \$5/sample if filtered, plus \$1500 for Hach spectrometer.	IT 1995; Medary 1992		Dr. Richard Medary U.S. Army Corps of Eng. 601 E. 12th Street Kansas City, MO 64106 (816) 426-7882	Large work area (2 large desks); requires the most setup time; possible TNB interference; no electricity or refrigeration required; must assemble materials; glassware must be rinsed between analyses.
ENVIROL		\$32/sample for TNT	Manufacturer only		ENVIROL, Inc. 1770 Research Way Suite 160 North Logan, UT 84341 435-753-7946	Self-contained kit; no additional solvent required.
DTECH	2 to 4 hours free on-site training.	\$30/sample for TNT or RDX plus \$300 for DTECHTOR (optional)	EPA 1995 (Methods 4050 and 4051); EPA 1997; Haas and Simmons 1995; Markos et al. 1995; Myers et al. 1994; Teaney and Hudak 1994	Calif. EPA 1996a and 1996b	Strategic Diagnostics, Inc. 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	Small working area; few setup requirements; no electricity or refrigeration required; temperature-dependent development time (effect can be reduced by changing DTECHTOR setting); significant amount of packing; relatively narrow range; no check on test; easy to transport or carry; kits can be customized. Out-of-range reruns require use of another kit.
Ideket Quantix	1 day free on-site training.	\$21/sample for TNT plus \$5880 for lab station or \$500/month rental.	EPA 1997; Haas and Simmons 1995; Markos et al. 1995		Ideket, Inc. 1245 Reamwood Ave. Sunnyvale, CA 94089 (800) 433-8351	Large work area (desk); requires setup time, electricity, refrigeration, and deionized water; requires careful washing of microwells; replicate run for each sample, average of the two is the result; less temperature dependent. Out-of-range reruns require use of another kit.

\*Expanded and modified from EPA 1997.

Table 3. Comparative data for selecting on-site analytical methods for explosives in soil\* (continued).

Method/ Kit	Training availability	Costs (not including labor)	Comparisons to Method 8330 references	Other references	Developer information	Additional considerations
Enviro- Gard	Free training available.	Plate: \$17/sample plus \$4129 for equip. and small supplies. Tube: \$20/sample plus \$2409 for equip. and small supplies.	Haas and Simmons 1995	Calif. EPA 1996c	Strategic Diagnostics, Inc. 375 Pheasant Run Newton, PA 18940 (800) 544-8881	Large work area (desk size); requires setup time, refrigeration, and power; acetone not supplied. Out-of-range reruns require use of another kit.
Ohmicron RaPID Assay	4 hours free on-site training.	\$13 to \$20/sample plus \$5500 for equip. (purchase) or \$800 for first month, \$400 each additional month (rental).	EPA 1997; Haas and Simmons 1995; Markos et al. 1995; Rubio et al. 1996	Calif. EPA 1996d	Strategic Diagnostics, Inc. 375 Pheasant Run Newton, PA 18940 (800) 544-8881	Large work area (desk); requires setup time, electricity, and refrigeration; less temperature dependent; low detection limit; all reagents supplied; reagents and kit need refrigeration. Out-of-range reruns require use of another kit.

\*Expanded and modified from EPA 1997.



mixing, and careful subsampling, resulted in an RSD of 11%. Because this field-mixing procedure was so effective in homogenizing the sample, the sampling and subsampling procedure is presented here (Jenkins et al. 1996a). Soil cores (0 to 15 cm in length and 5.6 cm in diameter) were collected into plastic resealable bags, and vegetation was removed. The sample of dry soil, a mixture of sand and gravel, was placed into 23-cm aluminum pie pans and was broken up using gloved hands; large rocks were removed (sieving may work well, too). A second pie pan was used to cover the sample, which was then shaken and swirled vigorously to disperse and homogenize the soil. The sample was then coned and quartered, and 5-g subsamples were removed from each quarter and composited to form the 20-g sample for analysis. Splits of the same sample were obtained by remixing the soil and repeating the coning and quartering.

Wilson (1992) studied sample preparation procedures for homogenizing compost prior to analysis for explosives. Wilson's (1992) method involves macerating air-dried compost using a No. 4 Wiley mill followed by sample splitting using a Jones-type riffle splitter. The improved method decreased the RSD from more than 200% to 3% for TNT analyses.

#### **Sample holding times and preservation procedures**

The EPA-specified holding time for nitroaromatic compounds in soil is 7 days until extraction, and extracts must be analyzed within the following 40 days (EPA 1995). The specified sample preservation procedure is cooling to 4°C. This criterion was based on professional judgment rather than experimental data.

Two significant holding time studies have been conducted on explosives (Maskarinec et al. 1991; Grant et al. 1993, 1995). Based on spiking clean soils with explosives in acetonitrile, Maskarinec recommended the following holding times and conditions: for TNT, immediate freezing and 233 days at 20°C; for DNT, 107 days at 4°C; for RDX, 107 days at 4°C; and for HMX, 52 days at 4°C. Grant spiked soils with explosives dissolved in water to eliminate any acetonitrile effects and also used a field-contaminated soil. The results on spiked soils showed that RDX and HMX are stable for at least 8 weeks when refrigerated (2°C) or frozen (-15°C) but that significant degradation of TNT and TNB degradation can occur within 2 hours without preservation. Freezing provides adequate preservation of spiked 2,4-DNT for 8 weeks or longer.

The results on field-contaminated soils did not show the rapid degradation of TNT and TNB that was observed in the spiked soils, and refrigeration appeared satisfactory. Presumably, the explosives still present in the field soil after many years of exposure are less biologically available than in the spiked soils.

Another study (Bauer et al. 1990) has shown that explosives in spiked, air-dried soils are stable for a 62-day period under refrigeration. Data from the Grant et al. (1993) study indicate that air drying of field-contaminated soils may not result in significant losses of explosives contaminants. Explosives in air-dried soils are stable at room temperature if they are kept in the dark.

Acetonitrile extracts of soil samples are expected to be stable for at least 6 months under refrigeration. Acetone extracts also are thought to be stable if the extracts are stored in the dark under refrigeration. (Acetone enhances photo-degradation of explosives.)

#### **Explosion hazards and shipping limitations**

The Department of Defense Explosive Safety Board approved the two-test protocol (Zero Gap and Deflagration to Detonation Transition tests) in March 1988 for determining the explosive reactivity of explosives-contaminated soil. Tests on TNT and RDX in sands with varied water content showed that soils with 12% or more explosives are susceptible to initiation by flame, and soils containing more than 15% explosives are subject to initiation by shock (EPA 1993). Explosives exist as particles in soil ranging in size from crystals to chunks, which can detonate if initiated. However, if the concentration of explosives is less than 12%, the reaction will not propagate. The water content of the soil has minimal effects on reactivity. The test results apply to total weight percent of secondary explosives such as TNT, RDX, HMX, DNT, TNB, and DNB. The tests do not apply to primary or initiating explosives such as lead azide, lead styphnate, and mercury fulminate. As a conservative limit, the EPA Regions and the U.S. Army Environmental Center consider soils containing more than 10% secondary explosives, on a dry weight basis, to be susceptible to initiation and propagation (EPA 1993). If chemical analyses indicate that a sample is below 10% explosives by dry weight, that sample is considered to be nonreactive. In most cases, this eliminates the requirement to conduct the expensive two-test reactivity protocol.

In sampling to determine whether an explosion

hazard exists, a biased sampling approach must be adopted (Sisk 1992). Soils suspected of having high concentrations of explosives should be grab-sampled and analyzed to determine whether the level of explosives exceeds 10%. Samples to be shipped for off-site analysis must be subsampled and analyzed on site. Explosives residues are usually concentrated in the top 5 to 10 cm of soil; therefore, deep samples must not be collected, blended, and analyzed to determine reactivity. Vertical compositing of surficial soils with high levels of explosives with deeper, relatively clean material provides a false indication of reactivity. Soils containing explosives residues over the 10% level can, using proper precautions, be blended with cleaner material to reduce the reactivity hazard and permit shipment to an off-site laboratory, but the dilution factor must be provided with the sample. If analytical results indicate that explosives are present at a concentration of 10% or greater, the samples must be packaged and shipped in accordance with applicable Department of Transportation and EPA regulations for reactive hazardous waste and Class A explosives (AEC 1994) to a laboratory capable of handling reactive materials.

In addition to the above information, the Army Environmental Center requires certain minimum safety precautions, as summarized below, for field sampling work at sites with unknown or greater than 10% by weight of secondary explosives contamination (AEC 1994). An extensive records search and historical documentation review must be conducted regarding the contaminated area to identify the specific explosives present, determine how the area became contaminated, estimate the extent of contamination, and determine the period of use. Personnel responsible for taking, packaging, shipping, and analyzing samples must be knowledgeable and experienced in working with explosives. Soil samples must be taken using nonsparking tools; wetting the sampling area with water may be necessary. If plastic equipment is used, it must be conductive and grounded. Sample containers must be chemically compatible with the specific explosive, and screw tops are prohibited. Samples are to be field screened for explosives if possible. Sufficient soil samples must be collected to characterize the site in a three-dimensional basis in terms of percent secondary explosives contamination with particular attention paid to identifying hot spots, chunks of explosives, layers of explosives, discolorations of the soil, etc.

In screening samples for reactivity, it should be remembered that most screening procedures test

for only one analyte or class of analyte. Without other supporting knowledge, concluding that a soil is not reactive based upon just one analysis could be dangerous. For assessing reactivity when multiple compounds are present at high levels, the CRREL and EnSys RISC colorimetric methods for TNT and RDX are more appropriate than immunoassay test kits because colorimetric tests detect a broader range of explosives analytes. Some conservatism in evaluating potential reactivity using colorimetric methods is appropriate. For example, Jenkins et al. (1996c) recommended using a limit of 7% explosives for conservatively estimating the lower limit of potential reactivity. High levels of explosives in soils may result in a low bias for on-site methods because of low extraction efficiencies. Colorimetric tests of chemical composition are used only to estimate potential reactivity. There are no on-site methods available to actually determine explosive reactivity. Explosive reactivity is a determination made from validated laboratory analyses.

#### **PROCEDURES FOR STATISTICALLY COMPARING ON-SITE AND REFERENCE ANALYTICAL METHODS**

When on-site methods are used, their performance needs to be evaluated; this is commonly done by analyzing splits of some soil samples by both the on-site method and a reference method (commonly Method 8330). The performance of the on-site method is then statistically compared to the reference method using a variety of methods, depending upon the objective and the characteristics of the data. In most cases, measures of precision and bias are determined. Precision refers to the agreement among a set of replicate measurements and is commonly reported as the RSD (standard deviation divided by the mean and expressed as a percent), the coefficient of variation (standard deviation divided by the mean), or the relative percent difference. Bias refers to systematic deviation from the true value.

The following discussion of statistical methods applies to comparisons of analytical results based on paired sample data, e.g., soil samples are analyzed by both an on-site method and a reference method, or soil extracts are analyzed by two different on-site methods. Care must be taken in interpreting the result. For example, if split subsamples from a soil sample are analyzed by on-site and reference methods, the differences de-

tected may be caused by subsampling error (sample was not homogeneous and the splits actually contained different concentrations of explosives), or differences in extraction efficiency (shaking with acetone versus ultrasonication with acetonitrile), rather than the analytical methods, which may also produce different results. However, if a group of acetone "extracts" are analyzed by two different methods, the subsampling and extraction errors are minimized and any significant differences should be from the analytical methods.

#### **Precision and bias tests for measurements of relatively homogeneous material**

When multiple splits of well-homogenized soil samples are analyzed using different analytical methods, statistical procedures described in Grubbs (1973), Blackwood and Bradley (1991), and Christensen and Blackwood (1993) may be used to compare the precision and bias of the methods. Grubbs (1973) describes a statistical approach appropriate for comparing the precision of two methods that takes into account the high correlation between the measurements from each method. An advantage of Grubbs' approach is that it provides unbiased estimates of each method's precision by partitioning the variance of the measurement results into its component parts (e.g., variance caused by subsampling and by the analytical method). Blackwood and Bradley (1991) extend Grubbs' approach to a simultaneous test for equal precision and bias of two methods. Christensen and Blackwood (1993) provide similar tests for evaluating more than two methods.

For comparisons involving bias alone, t-tests or analysis of variance may be performed. For comparing two methods, paired t-tests are appropriate for assessing relative bias (assuming normality of the data, otherwise data transformations to achieve normality must be applied, or nonparametric tests used). A paired t-test can be used to test whether the concentration as determined by an on-site method is significantly different from Method 8330 or any other reference method. For comparing multiple methods, a randomized complete block analysis of variance can be used, where the methods are the treatments and each set of split samples constitutes a block.

These tests are best applied when the concentrations of explosives are all of approximately the same magnitude. As the variability in the sample concentration increases, the capability of these tests for detecting differences in precision or bias decreases. The variability in the true quantities in

the samples is of concern, and high variability in sample results caused by poor precision rather than variability in the true concentration is well handled by these methods.

#### **Precision and bias tests for measurements over large value ranges**

When the concentrations of explosives cover a large range of values, regression methods for assessing precision and accuracy become appropriate. Regression analysis is useful because it allows characterization of nonconstant precision and bias effects and because the analysis used to obtain prediction intervals for new measurements (e.g., the results of an on-site method) can be used to predict the concentration if the samples were analyzed by a reference method.

In a regression analysis, the less precise on-site method is generally treated as the dependent variable and the more precise reference analytical method (e.g., SW-846 Method 8330) as the independent variable. To the extent that the relationship is linear and the slope differs from a value of 1.0, there is an indication of a constant relative bias in the on-site method (i.e., the two methods differ by a fixed percentage). Bias should be expected if on-site methods based on wet-weight contaminant levels are compared to laboratory methods based on the dry weight of soil samples. Similarly, an intercept value significantly different from zero indicates a constant absolute bias (i.e., the two methods differ by a fixed absolute quantity). There may, of course, be both fixed and relative bias components present.

When uncertainty is associated with the concentration of an explosive as measured by the reference method, standard least squares regression analysis can produce misleading results. Standard least squares regression assumes that the independent variable values are known exactly as in standard reference material. When the on-site method results contain appreciable error compared to the reference method, regression and variability estimates are biased. This is known as an errors-in-variables problem.

Because of the errors-in-variables problem, the slope coefficient in the regression of the on-site data on the reference data will generally be biased low. Hence a standard regression test to determine whether the slope is significantly different from 1 can reject the null hypothesis even when there is in fact no difference in the true bias of the two methods. A similar argument applies to tests of the intercept value being equal to zero.

To perform a proper errors-in-variables regression requires consideration of the measurement errors in both variables. The appropriate methods are outlined in Mandel (1984). These methods require estimating the ratio of the random error variance for the on-site method to that of the reference analytical method. With split sample data, suitable estimates of these ratios may generally be obtained by using variance estimates from Grubbs' test or the related tests mentioned above.

If the variance ratio is not constant over the range under study, more complicated models than those analyzed in Mandel (1984) must be employed. Alternatively, transformations of the data might stabilize the variance ratio. Note that it is the variance ratio, not the individual variances, that must remain constant. The ratio of variances for two methods with nonconstant absolute variances but constant relative variances will still have a constant variance ratio.

Two other caveats about the use of regression techniques also are appropriate. First, standard regression methods produce bias regression parameters estimation and may produce misleading uncertainty intervals. Similarly, the interpretation of R-squared values also is affected. Second, performing regressions on data sets in which samples with concentrations below the detection limit (for one or both methods) have been eliminated may also result in biased regression estimates, no matter which regression analysis method is used.

#### **Comparison to regulatory thresholds, action limits, etc.**

When the purpose of sampling is to make a decision based on comparison of results to a specific value such as an action level for cleanup, on-site and reference analytical method results may be compared simply on the basis of how well the two methods agree regarding the decision. The appropriate statistical tests are based on the binomial distribution and include tests of equality of proportions and chi-square tests comparing the sensitivity and specificity (or false positive and false negative rates) of the on-site method relative to the reference analytical method. Note that any measure of consistency between the two methods is affected by how close the true values in the samples are to the action level. The closer the true values are to the action level, the less the two methods will agree, even if they are of equal accuracy. For example, if the action level is 30 mg/kg and most samples have levels of above 1000 mg/kg, the agreement between the on-site method and ref-

erence should be very good. If, however, the concentration in most samples is 5 to 100 mg/kg, the two methods will be much more likely to disagree. This must be kept in mind when interpreting results, especially when comparing across different studies that may have collected samples at considerably different analyte levels.

#### **SUMMARY OF ON-SITE ANALYTICAL METHODS FOR EXPLOSIVES IN SOIL**

There is considerable interest in field methods for rapidly and economically determining the presence and concentration of secondary explosives in soil. Such procedures allow much greater flexibility in mapping the extent of contamination, redesigning a sampling plan based on near-real-time data, accruing more detailed characterization for a fixed cost, and guiding continuous remedial efforts. Ideally, screening methods provide high-quality data on a near-real-time basis at low cost and of sufficient quality to meet all intended uses, including risk assessments and final site clearances, without the need for more rigorous procedures. Although the currently available screening procedures may not be ideal (not capable of providing compound-specific concentrations of multiple compounds simultaneously), they have proved to be very valuable during the characterization and remediation of numerous sites. Currently, available field methods that have been evaluated against standard analytical methods and demonstrated in the field include colorimetric and immunoassay methods (Table 4). Each method has relative advantages and disadvantages, so that one method may not be optimal for all applications. To assist in the selection of one or more screening methods for various users' needs, Table 3 (modified and expanded from EPA 1997) provides information on on-site test kits for detecting explosives in soil. Selection criteria are discussed in the following sections.

The two types of currently available on-site methods, colorimetric and immunoassay, are fundamentally quite different. Both methods start with extracting a 2- to 20-g soil sample with 6.5- to 100-mL acetone or methanol for a period of 1 to 3 minutes, followed by settling and possibly filtration. The basic procedure in the CRREL and EnSys RISC colorimetric methods for TNT is to add a strong base to the acetone extract, producing the red-colored Janowsky anion. Absorbance is then measured at 540 nanometers (nm) using a spec-

**Table 4. Available on-site analytical methods for explosives in soil.**

<i>Analyte(s)</i>	<i>Test type</i>	<i>Developer/test kit</i>
A. Nitroaromatics	Colorimetric	CRREL,* EnSys RiSc
1. TNT	Colorimetric	CRREL, EnSys RiSc
	Colorimetric	USACE <sup>†</sup>
	Colorimetric	ENVIROL
	Immunoassay	DTECH
		Idetek Quantix
		Ohmicron RaPID Assay
		EnviroGard
2. TNB	Colorimetric	CRREL, EnSys RiSc
	Immunoassay	Ohmicron RaPID Assay
3. DNT	Colorimetric	CRREL, EnSys RiSc
4. Tetryl	Colorimetric	CRREL
B. Nitramines	Colorimetric	CRREL, EnSys RiSc
1. RDX	Colorimetric	CRREL, EnSys RiSc
	Immunoassay	DTECH
2. HMX	Colorimetric	CRREL, EnSys RiSc
3. NQ	Colorimetric	CRREL
C. Nitrate esters	Colorimetric	CRREL
1. NC	Colorimetric	CRREL
2. NG	Colorimetric	CRREL
3. PETN	Colorimetric	CRREL
D. AP/PA	Colorimetric	CRREL

\*U.S. Army Cold Regions Research and Engineering Laboratory.

<sup>†</sup>U.S. Army Corps of Engineers, Kansas City District.

trophotometer. The TNT concentration is calculated by comparing results to a control sample. The U.S. Army Corps of Engineers (USACE) and ENVIROL procedures use methanol for extraction, and the ENVIROL procedure uses solid phase extraction and liquid-liquid transfer, prior to reaction with base and formation of a colored anion. The RDX test has more steps.

The various immunoassay methods differ considerably in their steps; the DTECH method for TNT is the simplest. In the DTECH kit, antibodies specific for TNT and closely related compounds are linked to solid particles. The TNT molecules in the soil extract are captured by the solid particles and collected on the membrane of a cup assembly. A color-developing solution is added to the cup assembly and the presence (or absence) of TNT is determined by comparing the solution in the assembly cup to a color card or by using the simple field test meter. The color is inversely proportional to the concentration of TNT.

#### Method type, analytes, and EPA method number

The first criteria column in Table 3 lists the type of soil screening method, the analytes it detects, and the EPA SW-846 draft or proposed method number. A commercially available colorimetric kit,

EnSys RiSc, is used to determine TNT and RDX in soil. EnSys RiSc is the commercial version of the CRREL method for TNT and RDX. In addition to the CRREL method, USACE and ENVIROL developed colorimetric methods for TNT. EnSys RiSc and CRREL have additional colorimetric methods that can also be used to determine nitramines (HMX and NQ), nitrate esters (NC, NG, and PETN), and AP/PA. ENVIROL is developing an RDX colorimetric method that should be available in spring 1998.

Two companies, Idetek, Inc., and Strategic Diagnostics, Inc., manufacture commercial enzyme linked immunosorbent assay (ELISA) kits to detect TNT in soil. Idetek, Inc., produces the Quantix kit (both a plate and tube method are available), and Strategic Diagnostics, Inc., offers DTECH, EnviroGard, and Ohmicron RaPID Assay. DTECH kits are also available for RDX. Other explosives compounds can sometimes be detected using immunoassay kits because of their cross reactivity (see Interferences and Cross Reactivity section). The EnviroGard TNT immunoassay kit was formerly produced by Millipore Corp.

#### Detection limits and range

The lower detection limits of most methods are near or below 1 ppm. The detection range of a test

kit can be important: a broad range is generally more desirable. The importance of the range depends on the range of concentrations expected in samples, the ability to estimate the approximate concentration from the sample extract, the amount of effort required to dilute and rerun a sample, and the sampling and analytical objective. Some test kits have a range factor (upper limit of range/lower limit) of just one order of magnitude (10 $\times$ ), while other methods span two or more orders of magnitude (100 to 400 $\times$ ). Because explosives concentrations in soil may range five orders of magnitude (100,000 $\times$ ), reanalyzing many out-of-range samples may be necessary. The DTECH immunoassay methods require an additional test kit to run each sample dilution.

Other immunoassay methods can run dilutions in the same analytical run, but one must prepare the dilutions without knowing whether they are needed. The CRREL, USACE, and EnSys RiSc colorimetric procedures for TNT provide sufficient reagent to run several dilutions at no additional cost. For the EnSys RiSc TNT kit, the color developed can simply be diluted and reread in the spectrophotometer. The procedures that the test methods use for samples requiring dilution should be evaluated as part of the site-specific data quality objectives.

The detection range of a kit becomes much less relevant when the objective is to determine whether a soil is above or below a single action limit; the same dilution can be used for all samples. In some cases, changing the range of a kit may be desirable to facilitate decision-making. If a method has a range of 1 to 10 ppm and the contamination level of concern is 30 ppm, diluting all samples (using acetone or methanol or as directed by the instructions) by a factor of five would change the test kit range to 5 to 50 ppm and permit decisions to be made without additional dilutions.

Cleanup levels for explosives in soil vary considerably depending upon the site conditions, compounds present and their relative concentration, threats to groundwater, results of risk assessments, remedial technology, etc. (EPA 1993). Based on a review of data from many sites, Craig et al. (1995) suggested preliminary remediation goals of 30 ppm for TNT, 50 ppm for RDX, and 5 ppm for 2,4-DNT and 2,6-DNT.

#### **Type of results**

The type of results provided by the various screening methods are quantitative or semi-quantitative. The CRREL (TNT, RDX, and AP/PA),

EnSys RiSc, ENVIROL, USACE, Idetek Quantix, Ohmicron RaPID Assay, and EnviroGard (Plate) kits are quantitative methods, providing a numerical value. The CRREL 2,4-DNT method is considered semiquantitative and provides a somewhat less accurate numerical value. The DTECH and EnviroGard (Tube) test kits are semiquantitative (concentration range), and indicate that the level of an analyte is within one of several ranges. For example, the DTECH TNT soil kit, without dilution, indicates a concentration within one of the following ranges: less than 0.5, 0.5 to 1.5, 1.5 to 2.5, 2.5 to 4.5, 4.5 to 6.0, and greater than 6.0 ppm.

#### **Samples per batch**

Several of the available test kits are designed to run batches of samples or single samples or both. Using a test kit designed for analyzing a large batch to analyze one or two samples may not be very cost-effective or efficient. In most cases, samples may easily be batched for extraction and processed simultaneously.

#### **Sample size**

The size of the soil sample extracted contributes to the representativeness of a sample. Explosives residues in soil are quite heterogeneously distributed (Jenkins et al. 1996a, b; 1997), and as the subsample size actually extracted decreases, heterogeneity increases. Although sample preparation procedures such as drying, mixing, sieving, and splitting can reduce within-sample heterogeneity, such procedures can be time-consuming. Based on work by Jenkins et al. (1996b, 1997), field compositing and homogenization greatly improve sample representativeness. The commercial test kits use 2 to 10 g of soil, while the CRREL methods extract 20 g of soil to improve the representativeness of the results. For some test kits, it is possible to extract a larger sample using solvent and glassware not provided in the kit, and then using the required volume of extract for the analytical steps. The smaller the sample size, the more important is the homogenization of the sample before subsampling, although this procedure alone cannot completely compensate for loss of representativeness due to smaller samples.

#### **Sample preparation and extraction**

Soil extractions procedures for most of the screening methods are similar, shaking 2 to 20 g of soil in 6.5 to 100 mL of solvent (acetone or methanol) for 1 to 3 minutes. This may be followed by

settling or filtration or both. One test kit (EnviroGard) specifies air drying; for the EnSys RISC colorimetric test kits, drying to less than 10% moisture is optional. For the CRREL methods, samples must contain 2 to 3% water by weight; therefore, water must be added to the extract for very dry soils or incomplete color development will occur, resulting in a false negative.

The solvent extraction times of 1 to 3 minutes used in on-site methods may result in incomplete extraction of explosives compared with the 18-hour ultrasonic bath extraction step used in EPA Method 8330. The percent of explosives extracted is sample-specific but is generally higher for high concentration samples, higher for sandy soils, lower for clayey soils, and lower if 1-minute extractions are used relative to 3-minute extractions. For many soils, a 3-minute extraction time is adequate; ratios of 3-minute versus 18-hour extractions of TNT and RDX using acetone or methanol range from 66 to 109% as reported by Jenkins et al. (1996c). Jenkins recommends at least a 3-minute solvent extraction procedure for explosives. When pinpointing concentrations, a short kinetic study should be conducted of the specific soils encountered at a site (Jenkins et al. 1996c). The kinetic study would involve analyzing an aliquot of extract after 3 minutes of shaking, and again after 10, 30, and 60 minutes of standing followed by another 3 minutes of shaking. If the concentration of explosives increased significantly with the longer extraction time, a longer extraction period is needed. Jenkins et al. (1996a) found that 30-minute extraction times worked well for clay soils at the Volunteer Army Ammunition Plant, Chattanooga, Tennessee. Where multiple analytes are of interest in each sample, a common extract may be used for both the colorimetric and immunoassay test methods.

#### **Analysis time**

The analysis time or throughput for the colorimetric and immunoassay procedures ranges from 3 to 11 minutes per sample for batch runs. The EnviroGard kits specify air drying of samples (which would add considerable time), and drying is optional with the EnSys RISC colorimetric kits. Cragin et al. (1985) investigated various procedures for drying explosives-contaminated soils, including air, oven, desiccator, and microwave drying. Air and desiccator drying appear to result in only minor losses of explosives. Oven drying of highly contaminated soil (15% TNT) at 105°C for an unspecified period resulted in a 25% loss of

TNT; however, oven drying of less-contaminated samples for only 1 hour resulted in little loss of TNT, and 30 minutes of drying was estimated to be sufficient for analytical purposes. Microwave drying was not recommended because of spotty heating and drying. In addition, microwave drying should not be used because it may present a safety hazard and such drying degrades thermally unstable explosives in the soil. The effective production rate depends on the number of reruns required because a sample is out of the detection range.

#### **Interferences and cross-reactivity**

One of the major differences among the field methods is interference for colorimetric methods and cross-reactivity for immunoassay methods. The colorimetric methods for TNT and RDX are broadly class sensitive; that is, they are able to detect the presence of the target analyte but also respond to many other similar compounds (nitroaromatics and nitramines/nitrate esters, respectively). For colorimetric methods, interference is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. The ENVIROL colorimetric TNT method utilizes solid phase extraction and liquid-liquid transfer to reduce interferences from other nitroaromatics. Immunoassay methods are relatively specific for the primary target analytes that they are designed to detect. For immunoassay methods, cross-reactivity is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. The cross-reactive secondary target analytes for TNT are mainly other nitroaromatics. The cross-reactivity to these compounds varies considerably among the four TNT immunoassay test kits. The immunoassay test kit for RDX is quite specific, with only 3% cross-reactivity for HMX.

Depending upon the sampling objectives, broad sensitivity or specificity can be an advantage or disadvantage. If the objective is to determine whether any explosives residues are present in soil, broad sensitivity is an advantage. For the CRREL and the EnSys RISC colorimetric methods for TNT, the color development of the extracts can give the operator an indication of what types of compounds are present in soil; for example, TNT and TNB turn red, DNB turns purple, 2,4-DNT turns blue, 2,6-DNT turns pink, and tetryl turns orange. For the CRREL method and the EnSys RISC RDX kit, RDX as well as HMX, nitroglycerine, PETN,

and nitrocellulose turn pink. An orange color indicates that both TNT and RDX are present. Another advantage of the broad response of some colorimetric methods is they may be used to detect compounds other than the primary target analyte. For example, the colorimetric RDX methods may be used to screen for HMX when RDX levels are relatively low, and for NQ, NC, NG, and PETN in the absence of RDX and HMX. The USACE and ENVIROL colorimetric procedures are more specific to TNT than the CRREL and EnSys RISC colorimetric methods, but have not been as thoroughly evaluated. If a secondary target analyte is present at only low concentrations in a sample, the effect on the analytical result is minimal. If the objective is to determine the concentration of TNT or RDX when relatively high levels of other nitroaromatics and nitramines are present, immunoassay or the USACE or ENVIROL methods may be appropriate.

Extremes of temperature, pH, and soil water content can interfere with on-site analytical methods. According to the California Military Environmental Coordination Committee, the following physical conditions are generally not recommended for both colorimetric and immunoassay methods: temperatures outside the 4 to 32°C range, pH levels less than 3 or greater than 11, and water content greater than 30% (CMECC 1996). Specific product literature should be consulted for more information.

#### *Colorimetric methods*

For TNT methods, the primary target analyte is TNT, and the secondary target analytes are other nitroaromatics, such as TNB, DNB, 2,4-DNT, 2,6-DNT, and tetryl. For RDX methods, the primary target analyte is RDX, and the secondary target analytes are nitramines (HMX and NQ), and nitrate esters (NC, NG, and PETN). If the primary target analyte is the only compound present in soil, the colorimetric methods measure the concentration of that compound. If multiple analytes are present in soil, the CRREL and EnSys field methods measure the primary target analyte plus the secondary target analytes: nitroaromatics for the TNT test kit, and nitramines plus nitrate esters for the RDX test kits. Also, the response of the CRREL and EnSys colorimetric methods to the secondary target analytes is similar to that of the primary target analyte, and remain constant throughout the concentration range of the methods, although the observed colors may be different. The ENVIROL method is much less susceptible to interference

from other nitroaromatics because cleanup steps (solid phase extraction and liquid-liquid transfer) are used.

When several polynitroaromatic analytes are present in soil, the EnSys and CRREL colorimetric field results sum the analytes that respond to that test. For example, if a soil sample (as analyzed by Method 8330) contains TNT, TNB, RDX, HMX, and tetryl, the concentration estimate from the CRREL and EnSys RISC colorimetric methods for TNT would sum contributions from TNT, TNB, and tetryl, and the RDX test kit would sum contributions from RDX and HMX. Because response factors are not identical for each compound, the resulting concentrations will not quantitatively sum the analytes, but will provide an estimate that is adequate in light of the substantial spatial heterogeneity always encountered for these analytes in soil.

#### *Immunoassay methods*

For TNT kits, the primary target analyte is TNT, and the secondary target analytes are other nitroaromatics, such as TNB, DNTs, Am-DNTs, and tetryl. For the RDX kit, the primary target analyte is RDX, and there is cross-reactivity with HMX (3%). If the primary target analyte is the only compound present in soil, the immunoassay methods measure the concentration of that compound.

If multiple analytes are present in soil, the immunoassay kits measure the primary target analyte plus some percentage of the cross-reactive secondary target analytes. The response of immunoassay kits to the secondary target analytes is not equivalent to that of the primary target analyte. Also, the response does not remain constant throughout the concentration range of the kits. In addition, different immunoassay kits have different cross-reactivities to secondary target analytes based on the antibodies used to develop each method. Cross-reactivities for immunoassay kits are usually reported at the 50% response level ( $IC_{50}$ ), typically the midpoint of the concentration range of the kits. Table 5 shows the reported cross-reactivities at  $IC_{50}$  for the immunoassay kits. A complete cross-reactivity curve for the entire concentration range should be obtained from the manufacturers for the immunoassay kits being considered. Where multiple analytes exist in soil samples, immunoassay results may not directly compare with EPA Method 8330 results. For example, an immunoassay kit may have cross-reactivities of 23% for TNB and 35% for tetryl for the



Table 5. On-site analytical methods for explosives in soil, percent interference\* or cross-reactivity†.

Test method	Nitroaromatics								Nitramines		Other	
	TNT	TNB	DNB	2,4-DNT	2,6-DNT	2-AmDNT	4-AmDNT	Tetryl	RDX	HMX	PETN	
<b>TNT</b>												
CRREL	100	100	100	100	100	NC	NC	100	NC	NC		
EnSys RISC	100	100	100	100	100	NC	NC	100	NC	NC		
USACE	100		NC	NC								
DTECH	100	23		4		11	<1	35	<1	<1		
Idetek Quantix	100	47	1	2		0.5	2	6.5	<1	<1		
EnviroGard:												
Plate	100	7		2	41	<1	41	<1	<1	<1		
Tube	100	3		2	20	1	17	0.3				
Ohmicron RaPID	100	65	2	4	<1	3	1	5	<1	<1		
Assay												
ENVIROL	100	CL	CL	Pos	Pos	NC	NC	Neg	NC	NC	NC	NC
<b>RDX</b>												
CRREL	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100	100
EnSys RISC	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100	100
DTECH	<1	<1	<1	<1	<1	<1	<1	<1	100	3	<1	<1
<b>HMX</b>												
CRREL	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100	100
EnSys RISC	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100	100

\*Interference for colorimetric methods.

†Cross-reactivity for immunoassay methods at 50% response (IC<sub>50</sub>).

Blank cell = no data.

NC = No color development.

CL = Removed by cleanup steps.

Pos = Positive interference.

Neg = Negative interference.

TNT test kit, and 3% HMX cross-reactivity for the RDX test kit. The following simple example illustrates cross-reactivity, but in practice, it is not practical to calculate contaminant concentrations in this manner because of synergistic effects and because cross-reactivity is nonlinear. Using the same sample as the colorimetric example above, if a soil sample (as analyzed by Method 8330) contains 100 ppm each of TNT, TNB, RDX, HMX, and tetryl, the TNT field immunoassay kit would measure ~158 ppm (100 TNT + 23 TNB + 35 tetryl), and the RDX field method would measure ~103 ppm (100 RDX + 3 HMX). If the same sample did not contain tetryl, the TNT test kit would measure ~123 ppm (100 TNT + 23 TNB), and the RDX test kit would still measure ~103 ppm.

#### Matrix interferences

Both colorimetric and immunoassay methods may be subject to positive matrix interference from humic substances in soils, resulting in yellow extracts. For colorimetric methods, interference may be significant for samples containing less than 10 ppm of the target analyte. Through careful visual

analysis prior to colorimetric analysis, these interferences can be observed. Many of the immunoassay methods use a reverse coloration process, and humic matrix interference results in less color development, hence on-site method results are biased high as compared to laboratory results. Nitrate and nitrite, common plant nutrients in soil, are potential interferents with the CRREL and EnSys RISC colorimetric procedures for RDX. An extra processing step may be used to remove these interferents in soils that are rich in organic matter or that may have been recently fertilized.

The performance of field explosives analytical methods on other solid-phase environmental treatment matrices such as incineration ash, biotreatment residues such as compost or sludges from slurry phase bioreactors, cement-based solidification or stabilization material, or granular activated carbon from groundwater treatment systems, have not been extensively evaluated and will most likely be subject to matrix interferences or low extraction efficiencies. The performance of field methods on these matrices should be evaluated against laboratory methods on a site-specific basis.

### **Recommended quality assurance/quality control**

The recommended quality assurance/quality control (QA/QC) procedures vary considerably with the screening procedure. Some test methods do not specify QA/QC procedures and leave to the investigator the determination of the numbers of blanks, duplicates, replicates, and standards that are run. During field application of these methods, it is common to send at least 10 to 20% of the positive samples to an off-site laboratory for analysis by EPA Method 8330, and a smaller fraction of the nondetect samples also may be verified. In some cases, field methods are used to identify samples containing explosives residues. Samples containing explosives are sent for on-site analysis. In any case, the QC samples recommended by the method developer should be used.

While it is essential to ensure that field methods perform as intended, laboratory-type QC requirements may be inappropriate for on-site analytical methods. Because site characterization efforts may be cost constrained, excess QC samples reduce the number of field samples that can be analyzed. Because sampling error (variability) is typically much greater than analytical error (Jenkins et al. 1996a, b), especially for explosives residues, overall error is more effectively reduced by increasing the number of fields as opposed to the number of QC samples. Good sample preparation procedures and correlation of the field methods with the laboratory HPLC method over the concentration range of interest should be the primary performance criteria. Documentation of procedures and results must be emphasized.

During the initial evaluation of on-site and off-site analytical methods, it may be desirable to analyze a variety of QC samples to determine sources of error. The methods can then be modified to minimize error as efficiently as practical. This may involve collection and analysis of composite versus grab samples, duplicates, replicates, splits of samples, splits of extracts, etc. For more complete information on the types and uses of various QC samples, see *A Rationale for the Assessment of Errors in the Sampling of Soils* (EPA 1990).

### **Storage conditions and shelf life**

Storage conditions and shelf life of immunoassay kits are more critical than colorimetric methods. The reagents for some immunoassay kits should be refrigerated but not frozen or exposed to high temperatures. Their shelf life can vary from 3 months to more than 1 year. Colorimetric re-

agents can be stored at room temperature. The EnSys RISC colorimetric kits have shelf lives of at least 2 months and up to 1 or 2 years. Before ordering test kits, it is important to ensure that they will be used before the expiration date.

### **Skill level**

The skill level necessary or required to run these tests varies from low to moderate, requiring a few hours to a day of training. The manufacturers of the kits generally provide on-site training. A free training videotape on the CRREL TNT and RDX procedures (also useful for the EnSys RISC colorimetric kits) is available by submitting a written request to Commander, U.S. Army Environmental Center, Attn: SFIM-AEC-ETT/Martin H. Stutz, Aberdeen Proving Ground, MD 21010. Training videotapes are also available from some kit suppliers.

### **Cost**

As shown in Table 3, routine sample costs vary by method. The per-sample cost is affected by consumable items and instrument costs to run the method. In figuring costs per sample, it is important to include the costs of reruns for out-of-range analyses. With the EnSys RISC colorimetric TNT kit, the color-developed extract may be simply diluted and reread with the spectrometer. With all other methods, the original soil extract needs to be reanalyzed, which in the case of immunoassay procedures requires the use of another kit. Colorimetric methods typically have sufficient extra reagents to rerun samples with no increase in cost. It should be noted that the per-sample costs do not include labor hours.

### **Comparisons to laboratory method, SW-846 Method 8330**

The objectives of the study or investigation, the site-specific contaminants of concern, the concentration ranges encountered or expected, and their relative concentration ratios affect the selection of a particular on-site method. The accuracy of an on-site method is another selection criteria, but care must be used in interpreting accuracy results from comparisons between reference analytical methods and on-site methods.

Colorimetric methods actually measure groups of compounds (i.e., nitroaromatics or nitramines), and immunoassay methods are more compound specific. Therefore the reported accuracy of a method may depend on the mix of explosives in the soil and the reference method data used for

the comparison (i.e., data on specific compounds, or total nitroaromatics or nitramines).

The precision and bias of the screening methods are most appropriately assessed by comparison to established laboratory methods such as EPA Method 8330. Methods of comparison that have been used include relative percent difference (RPD), linear regression, correlation, coefficient of determination ( $r^2$ ), percent false positive and false negative results, analysis of variance, and paired t-tests. It should also be remembered that the contribution of analytical error is generally quite small compared to total error (field error is the major contributor).

Three studies have been conducted comparing the performance of two or more on-site methods with Method 8330. The procedures used in the studies for making the comparisons are given here and a summary of the results of each study follows. EPA (1997) calculated RPDs (the difference between the field and reference method concentration divided by the mean value and expressed as a percent), established a comparison criterion of 50% for RPDs, and determined the frequency with which various methods met that criteria within various sample concentration ranges. EPA (1997) also calculated regression lines and the  $r^2$ . Haas and Simmons (1995) compared on-site methods using the percentage of false positives and false negatives for determining whether samples were above or below two proposed remediation criteria for TNT in soil, 48 and 64 mg/kg. They also plotted regression data and reported calculated  $r^2$  values. Myers et al. (1994) calculated regression lines with 99% confidence intervals.

Although no study has compared all the field methods under the same conditions, the three studies evaluated multiple methods under slightly different field conditions (EPA 1997, Haas and Simmons 1995, Myers et al. 1994). Summary data from these studies are provided in Table 6. The table includes the intercept and slope of regression lines for TNT and RDX data for two concentration ranges, from the detection limit to 100 mg/kg and from 100 to 1000 mg/kg. Also included are the correlation coefficient ( $r$ ) and the mean RPD (absolute value of RPDs). The ideal regression line would have a slope of 1 and go through the origin (intercept of 0). The correlation coefficient ( $r$ ) shows the degree of association between the on-site method and Method 8330 and can range between -1 and +1. For a perfect positive correlation,  $r = 1$ . The mean RPD closest to 0 shows the greatest agreement with the reference laboratory

method. The RPDs presented are for TNT or RDX. The accuracy of colorimetric methods should improve when compared to total nitroaromatics or nitramines because the methods detect numerous related explosives. As the level of nitroaromatics other than TNT increases, the accuracy of the CRREL and EnSys RISc methods should appear to decrease. When compared to total nitroaromatics, however, the accuracy should increase. Thus, to attempt to identify the preferred screening method, it is important to determine specifically what analytical information is desired from a screening procedure and the relative concentration of the explosives at a site. Readers should consult the original studies for more details; however, some summary conclusions from the three cited studies follow.

The EPA (1997) study compared the CRREL, EnSys RISc, DTECH, Idetek Quantix, and Ohmicron RaPID Assay methods for TNT and concluded that "no single method significantly outperformed other methods" and accuracies for all the on-site methods were comparable. CRREL, EnSys RISc, and Ohmicron were more accurate in the greater-than-30-mg/kg TNT ranges, and DTECH was more accurate in the less-than-30-mg/kg range. The same study compared the CRREL, EnSys RISc, and DTECH methods for RDX in soil and concluded that they were slightly less accurate than the corresponding TNT methods.

Haas and Simmons (1995) evaluated immunoassay kits for TNT (DTECH, EnviroGard Tube and Plate, Idetek Quantix, and Ohmicron RaPID Assay). They concluded that for semiquantitative screening, all kits have the potential to accurately screen soil samples for contamination at risk-based levels (EPA 1993). The study found that, compared with HPLC analysis below 1 ppm, several of the assays had significant bias. Measurements near the detection limit are often problematic; above 1 ppm, the correlation between the immunoassay kits and HPLC was generally good.

Myers et al. (1994) evaluated and compared the EnSys RISc and DTECH methods for TNT in soil versus EPA Method 8330. The study found that EnSys demonstrated a good one-to-one linear correlation with reversed-phase high-performance liquid chromatography (RP-HPLC) that can be attributed to the procedure for extraction, i.e., a large sample size of dried homogenized soil. For the DTECH kit, comparison was more difficult because of the concentration range-type data and because one-to-one linear correlation with RP-

Table 6. Comparison of on-site analytical methods for TNT, RDX, and HMX to EPA Method 8330.

Method	Regression intercept	Regression slope	Correlation coefficient (r)	Mean RPD (absol. value)	Number samples	Reference
<b>MDL &lt; TNT ≤ 100 mg/kg</b>						
CRREL	10	0.84	0.74*	72	86	EPA 1997
EnSys RiSc	19	0.81	0.45*	90	123	EPA 1997
DTECH	2.9	0.79	0.76*	63	103	EPA 1997
Idetek Quantix	13	0.62	0.46*	84	124	EPA 1997
Ohmicron RaPID Assay	16	1.2	0.51*	97	115	EPA 1997
DTECH <sup>†</sup>	-17	6.7	0.81*	110	37	Haas and Simmons 1995
one outlier deleted <sup>†</sup>	3.7	2.4	0.91*		36	
EnviroGard plate <sup>†</sup>	13	1.3	0.79*	122	36	Haas and Simmons 1995
EnviroGard tube <sup>†</sup>	6.3	0.99	0.90*	95	21	Haas and Simmons 1995
Idetek Quantix <sup>†</sup>	36	2.1	0.39**	131	37	Haas and Simmons 1995
Ohmicron RaPID Assay <sup>†</sup>	18	1.8	0.83*	127	37	Haas and Simmons 1995
EnSys RiSc <sup>†</sup>	3.8	0.72	0.91*	56	12	Myers et al. 1994
DTECH <sup>†</sup>	5.4	0.94	0.30	88	10/11	Myers et al. 1994
<b>100 &lt; TNT &lt; 1000 mg/kg</b>						
CRREL	-25	1.4	0.67*	33	15	EPA 1997
EnSys RiSc	50	1.1	0.59*	57	21	EPA 1997
DTECH	-250	2.2	0.59**	60	17	EPA 1997
Idetek Quantix	210	0.09	0.30	65	22	EPA 1997
Ohmicron RaPID Assay	680	0.50	0.12	51	16	EPA 1997
<b>TNT &gt; 1000 mg/kg</b>						
EnSys RiSc	0	0.995	0.76	23	25	EPA 1997
<b>MDL &lt; RDX ≤ 100 mg/kg</b>						
CRREL	-1.2	0.56	0.89*	74	64	EPA 1997
EnSys RiSc	6.4	0.57	0.50*	61	114	EPA 1997
DTECH	2.7	0.20	0.49*	103	94	EPA 1997
DTECH <sup>†</sup>	-0.35	0.77	0.95*	66	27	Haas and Simmons 1995
<b>100 &lt; RDX &lt; 1000 mg/kg</b>						
EnSys RiSc	-9.9	0.68	0.50*	83	32	EPA 1997
DTECH	21	0.15	0.49**	127	25	EPA 1997
<b>RDX &gt; 1000 mg/kg</b>						
EnSys RiSc	0	0.38	0.64	75	19	EPA 1997
<b>MDL &lt; HMX &lt; 2200 mg/kg</b>						
CRREL	0	0.988	0.971*	—	76	Jenkins et al. 1997
EnSys RiSc	0	0.988	0.971*	—	76	Jenkins et al. 1997

\*Statistically significant at the 99% probability level.

<sup>†</sup>Statistics calculated from cited reference.

\*\*Statistically significant at the 95% probability level.

HPLC was poorer. Both methods were susceptible to interferences. Although both methods showed strong tendencies to cross-react with other nitroaromatics, sometimes resulting in false positives, neither method produced a false negative in a sampling of 99 soils. The study concluded that the EnSys RiSc kit was well suited for analyses

requiring good quantitative agreement with the standard laboratory method and that the DTECH kit was better suited for quick, on-site screening in situations where all samples above a certain range will be sent forward to a laboratory for confirmation by the standard method.

The ENVIROL test kit for TNT has only recently

been available, and no third-party evaluations of the performance of this kit have been reported thus far.

#### **Additional considerations**

Other important factors in the selection of an on-site method are the size and type of working area required, the temperature of the working area, the need for electricity and refrigeration, the amount of waste produced, the need to transport solvents, the degree of portability, etc. Immunoassay methods are more sensitive than colorimetric methods to freezing and elevated temperatures, and the ambient temperature affects the speed at which color development takes place on some immunoassay methods. Most tests are best run out of the weather, in a van, field trailer, or nearby building. High humidity has caused problems with clumping of the zinc dust in the colorimetric RDX tests.

#### **Emerging methods and other literature reviewed**

Several other screening procedures exist that have not been included in Table 3 because of the limited information available on published methods or commercial availability.

The Naval Research Laboratory Center for Bio/Molecular Science and Engineering has conducted developmental research on an antibody-based continuous-flow immunosensor for TNT and RDX and a fiber optic biosensor for TNT in water (Whelan et al. 1993, Shriver-Lake et al. 1995). Both methods have been evaluated as quantitative methods for explosives in groundwater at two sites (Craig et al. 1996). These methods reportedly tolerate a certain percentage of acetone, and are currently being evaluated for quantifying soil extracts containing explosives. Research of and instrument development for these methods are continuing.

The U.S. Army has been sponsoring the development of a cone penetrometer capable of detecting explosives in situ in soil, at levels determined to be 0.5 ppm in laboratory tests (Adams et al. 1995). Field tests have been conducted in which a probe is hydraulically pushed to depth by a 20-ton truck, samples are pyrolyzed in situ, and a sensor selective to nitrogen oxide is used to detect explosives. Research on this method is continuing.

A very simple spot test (colorimetric) kit can be assembled to detect elevated levels of TNT and RDX (>100 ppm) on filter paper swipes of surfaces and soil. Samples can be analyzed in 1 to 2 min-

utes at very low cost using the highly portable kit. This nonquantitative test kit was developed at Los Alamos National Laboratory and has been used to screen soil to ensure that explosives contamination does not exceed the 10% levels prior to shipping to an analytical laboratory for analysis (Baytos 1991, Haywood et al. 1995, McRea et al. 1995).

A semiquantitative method for identifying explosives using thermal desorption followed by ion mobility spectroscopy has been developed for security applications (Rodacy and Leslie 1992). The ion mobile spectroscopy method has been tested on small quantities of soil samples and is currently being evaluated for soil extracts (Atkinson et al. 1997). Research on this method is continuing.

The use of a mobile laboratory screening method for detecting high explosives has been described (Swanson et al. 1996). Ten-gram soil samples are extracted with 10 mL of acetone by shaking for 1 hour, and the extract is filtered. Analysis is by high performance liquid chromatography using a photo-array detector, and takes about 15 minutes per sample. It quantifies TNT, HMX, RDX, TNE, tetryl, 1,3-DNB, 2-AmDNT, 4-AmDNT, 2,4-DNT, 2,6-DNT, and all three NTs at detection limits of about 1 ppm.

A thermal desorption/Fourier transform infrared spectroscopy screening technique was under investigation by Argonne National Laboratory for the U.S. Army Environmental Center. The estimated detection limit was about 80 ppm without further modifications to the procedure (Clapper-Gowdy et al. 1992, Clapper et al. 1995), and no further research is being conducted.

Fast determination (100 samples/10 h/person) of explosives in soil (TNT, DNT, and NT) using thermal desorption followed by gas chromatography/mass spectrometry analysis has been reported. While no technical report on screening explosives in soil is available, the approach has been described in the literature for use with other contaminants (Abraham et al. 1993, McDonald et al. 1994).

An initial study was completed on the use of a simple thin-layer chromatographic method for use as a confirmation test following colorimetric-based procedures (Nam 1997). This method can be applied to extracts that test positive for TNT or RDX to discriminate among the several analytes that may be present.

A study was recently published where x-ray fluorescence was evaluated for use in screening for metals-containing primary explosives (Hewitt 1997).

Research is underway at CRREL to evaluate the use of solid-phase microextraction (SPME) for sampling the headspace vapor above a potentially contaminated soil for nitroaromatics. Initial results, where this sampling method is combined with gas chromatography with an electron capture detector, look promising, but the method will not work for nitramines such as RDX and HMX, because of their very low vapor pressures. The combination of SPME with IMS detection looks like a promising field option.

Another study at CRREL is investigating the use of gas chromatography with either a nitrogen-phosphorus detector or an electron capture detector as a method for analyzing acetone extracts in the field. The major advantage of this method would be the ability to determine the presence of the amino-dinitro transformation products. They are currently not detectable using the colorimetric or immunoassay methods.

#### SUMMARY OF THE EPA REFERENCE METHOD FOR EXPLOSIVES COMPOUNDS, METHOD 8330

##### Properties of secondary explosives

TNT and RDX have been the two secondary explosives used to the greatest extent by the U.S. military over the past 70 years. With their manufacturing impurities and environmental transformation products, the two compounds account for a large part of the explosives contamination at active and former U.S. military installations. While all of these explosives compounds can all be classified as semivolatile organic chemicals, their physical and chemical properties require different analytical approaches than normally used for other semivolatiles.

Table 7 presents some of the important physical and chemical properties for TNT and RDX, and some of their commonly encountered manufacturing impurities and environmental transformation products. The unique properties that differentiate these chemicals from other semivolatiles such as PCBs and polynuclear aromatic hydrocarbons (PNAs) are their thermal lability and polarity. Many of these compounds thermally degrade or explode at temperatures below 300°C. Thus, methods based on gas chromatography are not recommended for routine use. In addition, log  $K_{ow}$  values range from 0.06 to 2.01 compared with values of 4 to 5 for PCBs and PNAs, indicating that these compounds are quite polar and that normal non-polar extraction solvents used for other semivolatile organics may not elute successfully. For most routine analyses, environmental soil samples are extracted with polar solvents. The sample extracts are analyzed using RP-HPLC, often using SW-846 Method 8330 (EPA 1995).

##### Soil extraction

Extraction of TNT and RDX from soils has been studied in terms of process kinetics and recovery using methanol and acetonitrile with several extraction techniques including Soxhlet, shaking, and ultrasonication (Jenkins and Grant 1987). Acetone, while an excellent solvent for these compounds, was not included in this study because extracts were to be analyzed using RP-HPLC-UV, and acetone absorbs in the ultraviolet region used for detection of the contaminants of interest.

Overall, methanol and acetonitrile were found to be equally good for extraction of TNT, but acetonitrile was clearly superior for RDX. Equilibration of the soil with solvent using ultrasonication or a Soxhlet extractor appears to provide equivalent results; however, a subsequent investigation

Table 7. Physical and chemical properties of predominant nitroaromatics and nitramines.

Compound	Molecular weight	Melting pt. (°C)	Boiling pt. (°C)	Water solubility (mg/L at 20°)	Vapor pressure (torr at 20°)	log $K_{ow}$
TNT	227	80.1–81.6	240 (explodes)	130	$5.5 \times 10^{-6}$ at 25°	1.86
TNB	213	122.5	315	385	$2.2 \times 10^{-4}$	1.18
2,4-DNT	182	69.5–70.5	300	270	$1.4 \times 10^{-4}$	2.01
Tetryl	287	129.5	(decomposes)	80	$5.7 \times 10^{-9}$	1.65
RDX	222	204.1	(decomposes)	42	$4.1 \times 10^{-9}$	0.86
HMX	296	286	(decomposes)	5 at 25°	$3.3 \times 10^{-14}$	0.061
PETN	316	141	—	2.1 at 25°	$5.4 \times 10^{-9}$ at 25°	3.71

indicated that tetryl, another secondary explosive often determined in conjunction with TNT and RDX, is unstable at the temperatures required for Soxhlet extraction (Jenkins and Walsh 1994). That, combined with the ability to extract many samples simultaneously using the sonic bath approach, makes ultrasonication the preferred technique.

Results of extraction studies indicate that even when acetonitrile is used with ultrasonic extraction, the extraction is kinetically slow for weathered field-contaminated soils (Jenkins and Grant 1987, Jenkins et al. 1989). For that reason, SW-846 Method 8330 (EPA 1995) requires acetonitrile extraction in an ultrasonic bath for 18 hours.

#### **RP-HPLC determination (Method 8330)**

Generally, detection of the analyte within the proper retention-time window on two columns with different retention orders is required for confirmation of the presence of these explosives. Method 8330 specifies primary analysis on an LC-18 (octadecylsilane) column with confirmation on a cyanopropylsilane (LC-CN) column (Jenkins et al. 1989).

Walsh et al. (1973) were the first to report on the use of RP-HPLC for the analysis of nitroaromatics in munitions waste. Most subsequent HPLC methods for these compounds rely on ultraviolet detection because of its sensitivity and ruggedness. Initially, determination was specified at 254 nm because of the availability of fixed wavelength detectors based on the mercury vapor lamps and a significant absorbance of all target analytes at this wavelength. Current instruments are generally equipped with either variable wavelength detectors or diode array detectors, and wavelengths of maximum absorption can be selected to optimize detection. However, 254 nm is still often used because of the low incidence of interference at this wavelength.

#### **Method specifications and validation (Method 8330)**

Based on the research described above, SW-846 Method 8330 (EPA 1995) specifies the following:

1. Soil samples are air-dried and ground in a mortar and pestle for homogenization.
2. A 2-g subsample is placed in an amber vial, 10 mL of acetonitrile is added, and the vial is placed in a temperature-controlled ultrasonic bath for 18 hours.
3. The vial is removed from the bath and the soil is allowed to settle, a 5-mL aliquot is removed and diluted with 5 mL of aqueous  $\text{CaCl}_2$  to assist

in flocculation, and the diluted extract is filtered through a 0.45- $\mu\text{m}$  membrane.

4. A 100- $\mu\text{L}$  portion is injected into an HPLC equipped with a primary analytical column (LC-18) and is eluted with methanol/water (1:1) at 1.5 mL/min; retention times for the 14 target analytes range from 2.4 to 14.2 minutes.

5. If target analytes are detected, their presence is confirmed on a confirmation column (LC-CN).

6. The estimated quantitation limits in soil for most analytes is about 0.25 mg/kg, with RDX and HMX being somewhat higher at 1.0 and 2.2, respectively. No limits are provided for the AmDNs.

This procedure was subjected to a ruggedness test (Jenkins et al. 1989), and a full-scale collaborative test (Bauer et al. 1990) was conducted under the auspices of the Association of Official Analytical Chemists (AOAC). In addition to acceptance by the EPA Office of Solid Waste as SW-846 Method 8330 (EPA 1995), this procedure also has been adopted as Standard Method 991.09 by the AOAC (AOAC 1990) and as ASTM Method D5143-90 (ASTM 1990). In addition, the procedure has been used successfully by a large number of commercial laboratories for several years.

#### **SUMMARY**

A large number of defense-related sites are contaminated with elevated levels of secondary explosives. Levels of contamination range from barely detectable to levels over 10% that need special handling because of the detonation potential. Characterization of explosives-contaminated sites is particularly difficult because of the very heterogeneous distribution of contamination in the environment and within samples. To improve site characterization, several options exist: collecting more samples, providing on-site analytical data to help direct the investigation, sample compositing, improving homogenization of samples, and extracting larger samples. On-site analytical methods are essential to more economical and improved characterization. What they lack in precision and accuracy when used to simultaneously identify specific multiple compounds, the on-site methods more than make up for in the increased number of samples that can be analyzed. While verification using a standard analytical method such as EPA Method 8330 should be part of any quality assurance program, reducing the number of samples analyzed by more expensive

methodology can result in significantly reduced costs. Often 70 to 90% of the soil samples analyzed during an explosives site investigation do not contain detectable levels of contamination.

Two basic types of on-site analytical methods are in wide use for explosives in soil: colorimetric and immunoassay. The CRREL and EnSys colorimetric methods detect broad classes of compounds such as nitroaromatics or nitramines, while immunoassay methods and the ENVIROL colorimetric method are more compound specific. Because TNT or RDX is usually present in explosives-contaminated soils, the use of procedures designed to detect only these or similar compounds can be very effective.

Selection of an on-site analytical method involves evaluation of many factors, including the specific objectives of the study, compounds of interest and other explosives present at the site, the number of samples to be run, the sample analysis rate, interferences or cross reactivity of the method, the skill required, analytical costs per sample, and the need for and availability of support facilities or services or both. Another factor that may be considered is the precision and accuracy of the on-site analytical method, but it should be remembered that analytical error is generally small compared to field error, and that the precision and accuracy of a method is dependent on the site (compounds present and relative concentration) and the specific objectives (the question being asked).

Modifications to on-site methods may be able to improve method performance. In most cases, a larger soil sample can be extracted to improve the representativeness of the analytical sample. Also, with heavy soils or soils with high organic matter content, conducting a short-term kinetic study may be useful to determine whether a 3-minute extraction period is adequate. The shaking and extraction phase of all on-site methods should last at least 3 minutes. In all cases, a portion of the on-site analytical results should be confirmed by using a standard laboratory method. With appropriate use, on-site analytical methods are a valuable tool for characterization of soils at hazardous waste sites and monitoring soil remediation operations.

## POSTSCRIPT

During the preparation of this report, a series of corporate mergers have taken place, and the following kits are now the property of Strategic

Diagnostics Corporation (SDI), Newark, Delaware (telephone 302-456-6789): EnSys RISC, DTECH, Idetek Quantix, EnviroGard, and Ohmicron RaPID Assay. At the time of publication, only the EnSys RISC and DTECH kits are being offered on a routine basis. Discussions with SDI indicate that some of the other kits may be available by special order in the future, but potential customers are advised to contact SDI for up-to-date information.

Also, the ENVIROL TNT test became available and some information obtained from ENVIROL, Inc., has been inserted in this document. ENVIROL indicates that they are in the process of developing a colorimetric RDX test and that it will be available in spring 1998.

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